



Gold Adsorption By Alkaline Charcoal

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By
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Adsorbent Carbons for Many Industries

A Review of the Literature of This Broad Field Reveals Important
Properties of Specific Utility in Many Industrial Applications

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WHEN organic matter is decomposed under the proper conditions, the residue obtained is called charcoal. The decomposition is brought about (a) by heat, in the absence of oxygen, as in the distillation of wood; (b) by strong dehydrating agents, such as sulphuric acid, and (c) by certain types of bacterial action.

The residue obtained by heating wood out of contact with air is familiarly known as wood charcoal, whereas that from bones is called bone char. Wood charcoal has been used as a fuel for many centuries, but its more valuable properties were not early recognized. It was used to some extent as a deodorant, and Shenstone (1)* in 1854 is said to have used it in a respirator, the forerunner of our modern gas masks. Charcoal was used in the early stages of sugar refining as a clarifying agent, being replaced later by the more active products, bone char and blood char.

Only during the past few years have the latent possibilities of charcoal been recognized and their development begun. However, with the technical advances already made, coupled with the improvements certain to result from research, we can soon expect to have available, in large quantity, products not only much superior to animal carbons but performing services until recently believed impossible. Charcoal will ultimately be "mordanted" to serve a number of very important specific uses in the different industries.

The term "char" when used alone in this article will

*Numbers refer to references at the end of the article.

be taken to mean vegetable charcoal unless otherwise modified. Vegetable charcoal is, however, a generic term that requires further limitation, chiefly with regard to source and method of preparation. This is indicated in the following table:

Natural char.....	Anthracite coal, graphite, etc.				
Artificial char...	<table> <tr> <td>Hard...</td><td> - Sugar charcoal. - High-pressure wood charcoal. - Coconut hull, fruit-pit char. - Coke from coal, oil, etc. - Vulcanized fiber char. </td></tr> <tr> <td>Soft....</td><td> - Ordinary wood charcoal. - Cane bagasse, corn-stalk char. - Low-temperature lignite char. - Oil-shale char. - Rice hull or straw char. - Charred wood extracts. - Molasses char. </td></tr> </table>	Hard...	- Sugar charcoal. - High-pressure wood charcoal. - Coconut hull, fruit-pit char. - Coke from coal, oil, etc. - Vulcanized fiber char.	Soft....	- Ordinary wood charcoal. - Cane bagasse, corn-stalk char. - Low-temperature lignite char. - Oil-shale char. - Rice hull or straw char. - Charred wood extracts. - Molasses char.
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The natural chars will not be considered further, as they are not suited for activation as decolorizers. The manufactured chars are all artificial and relatively inactive as usually produced. The crude char must be treated by special methods in order to develop any of the general properties of decolorizing effect, gas adsorption, metal adsorption or catalytic effect.

Increasing any one of these properties is called "activation" of the char. From some of the recent literature one might be led to infer that activation of carbons refers only to gas adsorbents. These are relatively unimportant as compared with the decolorizing and clarifying carbons, both industrially and scientifically, and there is no occasion for limiting the broad meaning of the term activation to the specific class of gas adsorbents.

According to the uses of the activated char we have the three general classes:

(1) *Gas Adsorbents*—Usually prepared from the hard artificial chars. Most efficient in taking up noxious fumes, odors, hydrocarbon vapors, etc.

(2) *Color Adsorbents*—Usually prepared from the soft artificial chars. Most effective for decolorizing and clarifying solutions of dyes, oils, vegetable extracts, sirups, acids and as gas reaction catalysts.

(3) *Metal Adsorbents*—Soft artificial char. Used in removing gold, silver, platinum, etc., from solution.

It seems impossible to develop two of these general properties in the same char—for example, a good decolorizing char is only a moderate gas adsorbent and vice versa, although the essential difference in the two classes seems to be one of structure and not a difference in the form of the carbon. Furthermore, a metal adsorbent is usually a poor decolorizer. Decolorizing power and catalytic effect in certain gas reactions seem to be functions of the same general property of the carbon.

It can be shown that acid treatment of a metal adsorbent converts it into a decolorizing char. This indicates that the two classes are structurally identical. The decolorizing chars differ greatly in structure from the gas adsorbents and we know of no simple means by which they may be transferred from the one class to the other. The discussion to follow will deal with classes (2) and (3) only.

ADSORPTIVE PROPERTIES

If we eliminate gaseous adsorption together with inorganic adsorbents such as aluminum hydroxide or fullers earth, the literature on the theory of adsorption is fairly limited. The earlier experiments with chars were largely made with blood charcoal, bone charcoal and leather char—that is, materials mainly of animal origin. The effect of the materials associated with the char was not generally considered, although this is often the chief factor in deciding the value of a char for a given purpose. The effect of the mode of activation upon the chemical and physical properties of the char has been overlooked in other cases. Bartell and Miller (2) have carried out the only experiments on a char of unquestioned purity and arrive at some important conclusions. However, commercial chars are never pure carbon, hence the only safe method of approach is to know the history of the char. That will be the viewpoint throughout this paper.

The adsorptive properties of activated char are probably due to the same fundamental form of carbon, irrespective of the source of the char. These properties are to a considerable extent promoted or retarded by the presence of associated mineral matter fortuitously pres-

ent or added. The effect of chemical reagents depends on whether they are added before charring or are used in treating the crude primary char. In the category of such reagents must be included the atmospheric gases and the products of decomposition of the bodies present in the raw material.

Almost any vegetable substance can be converted into a decolorizing char. Thus we find mentioned in the patent literature, pine, birch and other woods, corn husks, cobs, stalks, cane trash, bagasse, peat, lignite, rice hulls, molasses, slop from alcohol extracts in paper pulp manufacture, ivory-nut shavings, oil shale, etc. It will be noticed that all of these materials fall in the class yielding soft, artificial chars. There is consequently loss in handling due to shattering and crushing. The production of a mechanically strong char is one of the present-day problems.

ACTIVATING VEGETABLE CHARS

The animal chars are fairly active in the primary form and may be used with no further treatment. Thus bone char was for many years considered as a unique substance—a belief that prevented progress in the development of the vegetable chars. As it contains considerable nitrogen and calcium phosphate, the decolorizing effect was ascribed to these compounds (3), (4), (5). The first attempts to produce active vegetable chars thus involved the addition of nitrogenous substances and phosphates to wood or peat followed by the calcination of the mixture (6), (7), (8). This idea has been shown to be erroneous, as the nitrogenous bodies simply control the form in which the carbon is deposited (22). From this standpoint the nitrogenous substances may be considered to fall in the class of accelerative reagents. In short, bone char owes its decolorizing power to the same form of carbon as occurs in wood charcoal. Mixing sawdust with fish scrap, bone oil, casein, phosphates, etc., will yield an active char only in so far as the added material affects the form of the deposited carbon.

Added materials may be listed according to their chemical or physical effects as follows:

(a) Those that act as dehydrating agents and bring about the decomposition at a very low temperature, and cause the decomposition products to be evolved as water

rather than as hydrocarbons. Among these may be mentioned zinc chloride, magnesium chloride and sulphuric acid.

(b) Those that provide a framework or skeleton for the deposition of carbon, protecting it from the cracked products of decomposition, and when dissolved out leave a porous mass of active char. Some materials as rice hulls contain a large proportion of silica in the natural state, whereas others require the addition of such substances as sodium chloride, sulphate and silicate, calcium acetate, carbonate, phosphate and sulphate or even silica itself.

(c) Those that have a chemical action on the products of decomposition, rendering them soluble or allowing them to escape freely. This prevents clogging of the pores and deposition of inactive carbon. Perhaps substances of this class are preferentially adsorbed by the active carbon liberated. The most notable substances in this class are the strong bases, as sodium or potassium hydroxides, or carbonates (9), (10), (11).

In the case of bone char, conditions of classes (a) and (c) are met by the substances present in the bones. The carbonate and to some extent the phosphate of calcium dissolve in dilute acids, exposing the carbon surfaces. The decomposition products of the cartilaginous substance do not crack appreciably and are freely evolved. Rice hulls, which contain very little nitrogen, yield a char that contains up to 50 per cent of silica and the primary char may be activated by boiling with 20 per cent of sodium hydroxide. The silica present fulfills condition (b) and possibly (c). However, in the case of pine wood, corn cobs or bagasse, it is evident that none of these conditions is met naturally. Hence, one of the addition agents must be used unless the primary char is to be activated by one of the processes to be considered later in this discussion.

A NEW TYPE OF CHAR

Nothing has been said as to the kind of char produced by the various addition agents, although it is known that two distinct kinds of char may be produced. If those substances that volatilize under 400 deg. C. are excluded, it will be noticed that those most effective are of the type of zinc chloride or magnesium chloride—in

other words, acidic bodies. Chars made in the presence of such compounds are active as decolorizers and need no further treatment except a thorough washing with water. On the other hand, sodium carbonate, potassium hydroxide or calcium oxide yield chars that are not very active if simply washed with water. However, by acid treatment they become approximately as effective as the best zinc-chloride char. Hence we may subdivide impregnating agents into those of acidic and those of basic nature. Chars made with substances in the first class are active color adsorbents as made, but chars made with basic materials require an acid wash to develop the activity. This is entirely aside from the extraction of the mineral filler by the acid as a solvent. The condition of the char is actually changed.

Decolorizing chars are, as a rule, either neutral or acid washed, since they are commonly used in solution in which the color exists as an acid radical. The chars made with alkaline agents will likely prove valuable in certain types of work in which an alkaline condition is required, although this point has not been settled experimentally. They have been shown to be the most efficient metal absorbents thus far discovered. This point has not been stressed before, hence the properties of the alkaline activated chars deserve, and will receive, full discussion by the present author.

The remaining methods of producing activated char, of either the adsorbent or gas type, are based on the theory that the primary char obtained by heating vegetable matter is inactive, because the active carbon at first set free is coated over, or gas treated, by the decomposition products at higher temperatures (12), (13). Also active carbon is set free in only a limited range of temperature, preferably below 600 deg. C. This explains the value of addition agents that promote decomposition at lower temperatures. Gas coke, gas black and graphite, being formed at high temperatures, are not subject to activation.

In order to eliminate the coating of inactive material, selective oxidation of the primary char, by either air or mixtures of air and carbon dioxide at about 400 deg. C., or steam at 900 to 1,000 deg. C., is resorted to. If the decomposition products are oxidized during the period of carbonization, they do not become stabilized and the

best chars are probably made under slight oxidizing conditions throughout the time of heating.

The adsorbed complexes have been removed by solvents with some success. (U. S. Pat. 1,423,231 claims the use of selenium oxychloride for this purpose.) Such ordinary solvents as benzene or gasoline are of no value for this method.

Coates (14) activated charcoal simply by heating it to 1,200 deg. C. for a prolonged period. The method attempted to volatilize the hydrocarbons adsorbed by the active carbon. It is believed that any activation so obtained is due to infiltration of air (2), (22). Moreover, the temperature employed would tend to decrease the activity due to the transformation into inactive or partly graphitized form of carbon. Herbst (15) has given perhaps the only indication of this change in his study of the change of electrical conductivity of charcoal with temperature. At 1,150 deg. C. the conductivity changes very rapidly (16).

The production of a decolorizing carbon by selective oxidation appears to be an exception to the rule that decolorizing chars are acid treated. However, an oxidized char is extremely sensitive to acidic conditions, and unless the char is protected by an alkaline ash the adsorption of carbon dioxide or other acidic constituents of the furnace gases during cooling is usually sufficient to bring about the necessary changes. This point is brought out clearly by the experimental work of Bartell and Miller (2) and is indicated in the technical practice (17) of quenching charcoal while hot in order to increase the metal precipitating power. One of the functions of an alkaline impregnating agent in the production of a metal adsorbent char may be to protect the char from the influence of acidic substances during the

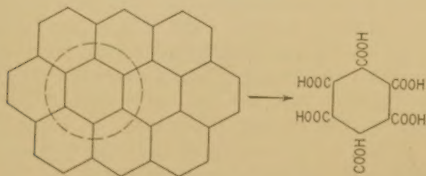


Fig. 1—Oxidation of Carbon Complex to Mellitic Acid

time of cooling. However, an air-oxidized char is not converted into a metal precipitant by boiling with a solution of sodium hydroxide, hence the effect of the alkali is something more than to act as a buffer material.

Structure of Active Charcoal

Previous to 1913 Coates had reached the conclusion that low-temperature distillation of wood was necessary to the production of an effective decolorizing char. Chaney's theory (12), derived from the results of experiments made during the war, may be considered as an interpretation of the same experimental fact. Empirically, then, we may conclude that first stage charring at low temperature is an established necessity. What is the nature of the product so obtained?

Cross and Bevan (18) stress the fact that low-temperature charcoal may hardly be considered as a form of carbon. They propose the term "pseudo-carbons" for products obtained, for example, by the action of sulphuric acid on sugar. Verneuil (19) has shown that when oxidizing agents, such as sulphuric acid, act on wood charcoal, the products obtained are not those we get with pure carbon. He isolated mellitic acid $C_6(COOH)_6$ and pyro-mellitic acid $C_6H_2(COOH)_4$ from the reaction products. The char used showed the analysis $H_2 = 2.55$ per cent, $O_2 = 8.38$ per cent and $C = 87.62$ per cent. Charcoal that had been heated to a white heat was not acted upon. Meyer (20) concluded therefore that the mellitic acid is a product obtained from the hydrocarbons present, since the yield varied from 40 per cent to 0 per cent as the temperature of heating was increased. Although the amount of hydrogen present in wood charcoal is more than sufficient to account for the yields from the low-temperature char, it remains to be explained why the yield falls to zero with the char heated to a white heat. Such char is shown to contain up to 0.6 per cent of hydrogen, which is sufficient to give a 25 per cent yield of mellitic acid.

It is believed that the real explanation lies in the oxidation of the carbon complexes, as shown in the sketch in Fig. 1. It is evident that the decreased yield of mellitic acid cannot be ascribed simply to the loss of hydrocarbons on heating. The zero yield with highly heated char is probably a function of the changed car-

bon linkages that also account for the change in density, greater resistance to oxidation and less adsorptive power. The modification of charcoal produced at higher temperatures likely bears the same relation to the low-temperature form that the modifications of such products as alumina and ferric hydroxide produced at high temperatures bear to the forms obtained at low temperatures. These substances undergo a similar change in crystalline form, density and the adsorptive power. It will be shown in a later paper that low-temperature chars act very much like colloids and may be coagulated from suspensions by the addition of acids.

It is believed that the active form of carbon simply represents an unorganized or less complex state of free carbon, whereas that set free at higher temperatures at once assumes a stable arrangement due to the greater energy conditions existing at the moment of decomposition and hence is inactive as an adsorbent. There is some evidence for believing in a third form of carbon in addition to that of graphite and diamond, but not more, as would be required to explain the existence of an alpha and beta form of the so-called amorphous carbon. However, the deviations among the forms of diamond, graphite and purified charcoal with regard to their physical properties is almost sufficient evidence. Copisarow (21) comes to the same conclusions, although his work is highly speculative, through a study of the possible molecular configurations of carbon.

The following include most of the more important patents referred to in this discussion:

PATENTS

- (1) Mumford, U. S. Pats. 1,286,187; 1,287,592; 1,314,203; 1,314,204; 1,359,094.
- (2) Weinrich, U. S. Pat. 1,308,826.
- (3) Zerban, U. S. Pat. 1,290,002.
- (4) McKee, U. S. Pats. 1,133,049; 1,372,971.
- (5) Demme, U. S. Pat. 1,249,041.
- (6) Knopfelmacher, U. S. Pat. 1,358,162.
- (7) Ostrejko, U. S. Pat. 1,362,064.
- (8) Meister Lucius & Bruning, D. R. Pat. 371,691.
- (9) Zellstoff Fabrik Waldhoff, D. R. Pat. 309,155.
- (10) Degener, D. R. Pat. 44,063.
- (11) Zeiniczek, Austrian Pat. 3,718.
- (12) Bonnard, Holl. Pat. 3,149.
- (13) Hudson, Brit. Pat. 139,156.
- (14) Eastick, Brit. Pat. 136,873.
- (15) Hayasha, Brit. Pat. 121,035.
- (16) Leadbeater, Brit. Pat. 122,698.
- (17) China Sugar Co., Brit. Pat. 124,638.
- (18) Tai-Koo Sugar Co., Brit. Pat. 125,230.
- (19) DeBruyn, Ltd., Brit. Pat. 162,117.
- (20) Penrose, Brit. Pat. 122,465.

- (21) Shilstone, Brit. Pat. 116,253.
- (22) Inada, Jap. Pat. 35,876.
- (23) Swzuki, Jap. Pat. 34,755.

REFERENCES

- (1) Shenstone, *Pharm. J.*, vol. 13, p. 454 (1854).
- (2) Bartell and Miller, *J. Am. Chem. Soc.*, vol. 44, p. 1866; vol. 45, p. 1106 (1923).
- (3) Wallace, *Proc. Glasgow Phil. Soc.*, vol. 6, p. 377 (1865).
- (4) Patterson, *J. Soc. Chem. Ind.*, vol. 22, p. 608 (1903).
- (5) Hall, *J. Ind. Eng. Chem.*, vol. 14, p. 18 (1922).
- (6) Facilides, *Arch. Pharm.*, vol. 141, p. 121 (1870).
- (7) Von Melsens, *Pol. Notizbl.*, vol. 30, p. 281 (1874).
- (8) Zerban, *Bull. Louisiana Exp. Sta.*, No. 167.
- (9) Bonnet, *Chem. Age (N. Y.)*, vol. 31, p. 372 (1923).
- (10) Peck and Adams, *Louisiana Planter*, vol. 61, p. 395 (1918).
- (11) Daude, *Z. Ver. Deut. Zuckerind.*, vol. 71, p. 13, (1921).
- (12) Chaney, *Trans. Am. Electrochem. Soc.*, vol. 36, p. 91 (1919).
- (13) Ray, *Chem. & Met.*, vol. 28, p. 977 (1923).
- (14) Coates, *Bull. Louisiana Exp. Sta.*, No. 161.
- (15) Herbst, *Biochem. Z.*, vol. 115, p. 204 (1921).
- (16) Phillips, *J. Chem. Soc.*, vol. 117, p. 362; vol. 118, p. 699 (1920).
- (17) Edmands, *Bull. Inst. Min. & Met.*, London, March, 1918.
- (18) Cross and Bevan, *Phil. Mag.*, vol. 13, p. 325 (1882).
- (19) Verneuil, *Compt. rend.*, vol. 132, p. 340 (1901).
- (20) Meyer, *Monatsch.*, vol. 35, p. 163 (1914).
- (21) Copisarow, *Chem. News*, vol. 118, p. 310 (1919).
- (22) Horton, *J. Ind. Eng. Chem.*, vol. 15, p. 519 (1923).

A New Class of Activated Carbons

Alkaline Impregnated Chars, Peculiarly Adapted for Metal Adsorption, Show Many Properties Commonly Ascribed to Colloids

BLACK ash residue (the material left after extracting the calcined liquors from the soda-pulp process for manufacturing paper pulp) is an alkaline char and can be used directly as a decolorizing char in strongly acid liquors. However, for use in cane sugar solutions where approximate neutrality is always maintained, it is practically inert unless previously acid treated. The strength of acid employed is immaterial if it is above a certain low limit. This point is observed in technical practice by adding acid to the alkaline char suspended in water and noting the point where the suspension "clears" or begins to settle rapidly. The finely ground alkaline char will remain in suspension for several days, but upon adding acid it will settle in a few minutes. Further addition of acid beyond this point improves the char very little if any.

The results obtained by plotting the time of settling against the acidity of suspensions of alkaline sugar char are shown in Fig. 1. This char was prepared by dissolving 100 grams of sugar and 20 grams of sodium carbonate in a little water and then gradually raising the heat to 600 deg. C. The resulting char was washed as free from alkali as possible, dried and ground to pass through a 100-mesh sieve. This material is a soft, velvety black char and not the usual hard, shiny char obtained by heating sugar alone. The chars used in the settling test were filtered out, washed and dried. The p_H of the suspensions was measured with the quinhydrone electrode at 25 deg. C.

The decolorizing power of the dried char from these tests was determined in a neutral caramel solution by the method already described by one of the present writers (Horton). The results are plotted in Fig. 2. It should be noted that, although the char giving maximum efficiency has been treated with acid of p_H 3.5, it was previously washed and dried before testing. Actually when this char is suspended in water the reaction is between p_H 4 and p_H 5.5 and not p_H 3.5, as might be expected. That this is a general case will be shown later.

An assortment of chars were next washed thoroughly, dried and suspended for 24 hours in distilled water (2 grams per 100 c.c.). After filtering out the carbons, the p_H of the filtrate was measured with the quinhydrone electrode at 25 deg. C. The results are shown in Table I. An interesting feature of this series of tests is that all the chars had been washed on a Buchner funnel until the runnings were neutral to litmus paper or nearly p_H 7.

Item 2 represents a sample taken from 100 grams of 200-mesh black ash residue boiled up with successive portions of 1,000 c.c. of distilled water and filtered, until the filtrates totaled about 50 liters. This indicates the futility of trying to wash a char commercially to a given reaction using pure water. Furthermore, the chars seem to group in three classes, of which the examples given are representative. Those made with alkali and heated to 500-600 deg. C. seem to wash more nearly neutral, those heated to 900 deg. C. or above seem to retain the alkali and have a fixed reaction of about p_H 8, while the acid-washed chars give a value of about p_H 4.5. This method used with caution will throw considerable light on the nature of an unknown char and the nature of the treatment it has received.

The action of the various chars under the influence of an electrical field is interesting. The alkaline chars when suspended in pure water move toward the positive pole, whereas the acid-treated chars are practically stationary. This indicates that the alkaline chars are negatively charged and that the acid-treated chars are neutral or at the isoelectric point. The ability of a decolorizing char to adsorb either acid or basic colors is thus explained. Cane juice is decolorized in slightly acid solution, while cottonseed oil is usually made

Table I—Reaction of Filtrates From Various Chars

Char	p_H of Filtrate
(1) Black ash residue, washed.....	8.25
(2) Black ash residue, extra washed.....	8.20
(3) Sugar char made with sodium carbonate and heated to 900 deg. C	8.34
(4) Pine char made with sodium carbonate and heated to 600 deg. C	7.38
(5) Sugar char made with sodium hydroxide and heated to 500 deg. C	7.23
(6) Water used.....	6.1
(7) Commercial Norit.....	8.23
(8) Acid-washed Norit.....	4.30
(9) Commercial Darco.....	4.98
(10) Black ash residue, acid washed.....	4.26

alkaline in order to be decolorized. The char assumes the opposite sign to the body adsorbed.

It will thus be seen that a char made with soluble alkaline impregnating agents, such as sodium carbonate, and then thoroughly washed will be practically inert in a neutral or only slightly acid solution. If this char is previously treated with acid and washed (and even ignited to red heat), it now behaves as a normal decolorizing char. This change in the nature of the char is fundamental and has nothing to do with the question of the reaction of the medium to be decolorized. In other words, the char has been conditioned to act in a specific manner. This point has been very generally ignored in the study of decolorizing chars. However, the original alkaline char is very effective as a metal adsorbent, which property is practically lost on treatment with acid and is not regained by treating the char with an aqueous solution of an alkali.

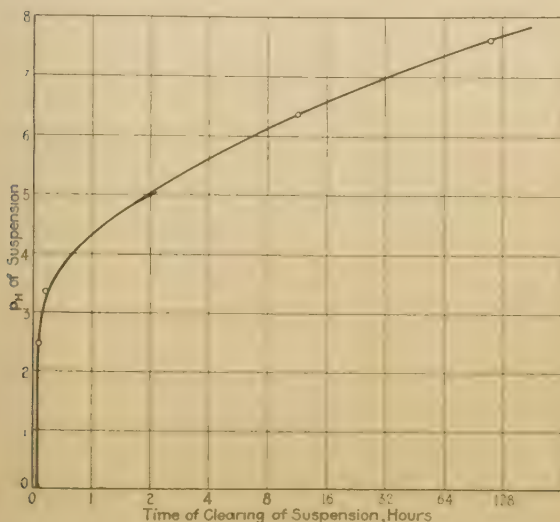


Fig. 1—Effect of Acidity on the Settling of Alkaline Char

It will be observed that the effect of the acid reaches a maximum at p_H 4 to 3.4. This might be called "the clearing point" of the char.

FACTORS FAVORING METAL ADSORPTION

Mainly because of lower cost and greater ease of determination, solutions of copper salts were used in the preliminary study of metal adsorption. However, copper is by no means as easily adsorbed from solution as gold; hence variations in the char toward increased copper adsorption represent a considerable increase in the gold adsorption. In fact, a char having no copper-precipitating power may even be fairly effective in an aurocyanide solution.

In order to determine the effect of acid treatment on copper adsorption by alkaline charcoal, the remaining portions of the char samples used for the clearing time experiments were treated with solutions of copper sulphate. The method employed in all of the following

Table II—Effect of Acidity on Cu Adsorption

Original Concentration of Solution Gram Cu Per 100 c.c.		Per Cent of Copper Adsorbed	r_H of the Filtrate
0.5997		3.4	4.37
0.5997		1.7	4.22
0.5997		0.6	3.73
0.5997		0.3	1.66

tests was briefly this: a 1.0000-gram sample of the char was suspended in 100 c.c. of approximately 0.1 molar copper sulphate solution for 24 hours. The char was then filtered off through a dry paper and the first 20 c.c. discarded. The remaining filtrate was mixed and a 25-c.c. aliquot titrated for copper. The iodide and cyanide procedures were used with practically the same results.

The effect of acid treatment is indicated in Fig. 3 and is more strikingly demonstrated in the following experiment:

Solutions containing varying amounts of added acid and a constant concentration of copper were treated with 100-mesh black ash residue and both the concentration change of copper and the p_H of the filtrate determined. The results are given in Table II and plotted in Fig. 4.

Decreasing acidity would appear to be favorable to metal precipitation by char. This effect cannot be pursued into the alkaline range, since copper would be chemically precipitated. On the other hand, if an

Table III—Effect of Ammoniacal Solution on Cu Adsorption

Char	Solution	Per Cent of Copper Adsorbed
Black ash residue	CuSO_4	27.7
Black ash residue	$\text{CuSO}_4 + \text{NH}_4\text{OH}$	10.0
Sugar char 500° C.	CuSO_4	26.6
Sugar char 500° C.	$\text{CuSO}_4 + \text{NH}_4\text{HO}$	8.4
Sugar char 900° C.	CuSO_4	25.7
Sugar char 900° C.	$\text{CuSO}_4 + \text{NH}_4\text{OH}$	5.6
Black ash residue	$\text{CuSO}_4 + \text{KCN}$	Trace only

Original solution = 0.3448 gram copper per 100 c.c.

alkali such as ammonium hydroxide is added which forms a soluble complex in alkaline solution, the effect of decreasing acidity is overbalanced by the decreased

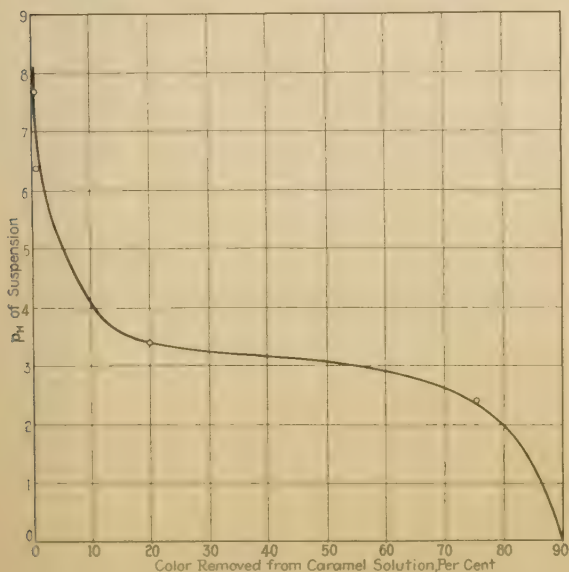


Fig. 2—Decolorizing Power of Char from Sugar

The maximum activity is reached with a char that has been suspended in an acid of about p_H 3.5, which corresponds closely with the clearing point indicated in Fig. 1.

copper-ion concentration or activity. Hence, we should expect to find little adsorption in an ammoniacal solution and practically none in a cuprocyanide solution.

The copper-ion concentration (activity) in the latter solution is extremely low. The results of a few tests in this direction are given in Table III.

The next point of interest is the variation in copper adsorbed with the concentration of copper in solution. This is best illustrated with an adsorption isotherm. In addition to the change in concentration, we have determined the p_H of the original solution and the filtrate. The results of one set of measurements at 25 deg. C. are given in Table IV.

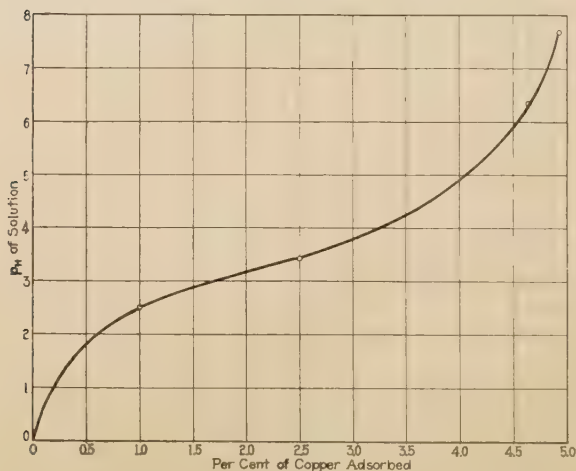


Fig. 3—Effect of Acid Treatment on Copper Adsorption

This adsorption curve shows no marked transition, yet in the case of chars treated with acid stronger than p_H 4, the copper drops off rapidly.

The percentage of copper adsorbed is plotted against the original concentration in Fig. 5. This appears to have the ordinary form of an adsorption curve. However, it should be noted that in case the adsorption is less than 5 per cent, the concentration plays no part. In Fig. 5 are also plotted the p_H of both the original solution and the filtrates. In the more concentrated solutions the filtrate is less acid than the original solution by a constant amount (about 0.62 p_H) until the adsorption becomes 5 per cent or greater. After this point is reached the acidities of the solution and filtrate

approach each other and at about 20 per cent adsorption they are the same, or there is no change in acidity during adsorption. It is believed that the explanation of these facts does not lie in the relative amounts of copper adsorbed as much as in the acidity of the original

Table IV—Variation in Cu Adsorption With Solution Concentration

Concentration Original Solution (Grams of Cu Per 1,000 c.c.)	Concentration Filtrate	Per Cent of Copper Adsorbed	p_H of the Filtrate
73.185	72.340	1.10	3.76
54.888	54.060	1.51	3.92
36.592	35.836	2.07	4.02
18.296	17.636	3.60	4.17
10.977	10.540	3.95	4.29
7.318	6.854	6.42	4.35
3.659	3.230	11.6	4.45
1.829	1.530	15.7	4.54
0.732	0.476	36.5	4.81

Table V—Effect of Heating Time on Cu Adsorption

Black ash residue impregnated with 1 per cent sodium carbonate heated at 950 deg. C.

1 hour gave.....	5.43 per cent copper adsorbed
2 hours gave.....	5.40 per cent copper adsorbed
3 hours gave.....	5.40 per cent copper adsorbed
4 hours gave.....	5.49 per cent copper adsorbed
5 hours gave.....	5.41 per cent copper adsorbed
7 hours gave.....	5.38 per cent copper adsorbed

Table VI—Effect of Alkali Concentration on Cu Adsorption

Black ash residue heated for 1 hour at 950 deg. C. with

0.0 per cent sodium carbonate gave.....	5.35 per cent copper adsorbed
0.5 per cent sodium carbonate gave.....	5.26 per cent copper adsorbed
1.0 per cent sodium carbonate gave.....	5.31 per cent copper adsorbed
3.0 per cent sodium carbonate gave.....	5.38 per cent copper adsorbed
5.0 per cent sodium carbonate gave.....	5.35 per cent copper adsorbed
10.0 per cent sodium carbonate gave.....	5.35 per cent copper adsorbed

Table VII—Effect of Alkaline Activation on Different Chars

Char	Conc. of Filtrate Gram Cu Per 100 c.c.	Per Cent of Cu Adsorbed
Crude sugar char.....	0.6531	-2.5 }
Treated sugar char.....	0.6186	+2.5 }
Crude pine char.....	0.6450	-1.4 }
Treated pine char.....	0.6364	-0.06 }
Crude black ash residue.....	0.6032	+5.1 }
Treated black ash residue.....	0.5992	+5.8 }

Conc. of original solution = 0.6360 gram per 100 c.c.

solution. If the copper sulphate solution is more acid than about p_H 3.5 to p_H 3.8, the char is at once deactivated, the copper is only slightly adsorbed and the alkali in the char simply reacts in a chemical way with the free acid in the solution. There are various ways of looking at this matter, however, and about the only valid deduction we may draw is that acidity due to hydrolysis will affect the adsorption if it is above a certain point. This may explain certain erratic values noted in the literature.

In U. S. Patent 1,372,971 of McKee it is stated that the metal-adsorbing power of ordinary wood charcoal is greatly increased by an alkaline treatment at moderately elevated temperatures. The following are the results of an attempt to activate various carbons in this manner:

The first carbon treated was black ash residue, a carbon which in the process of making has been heated

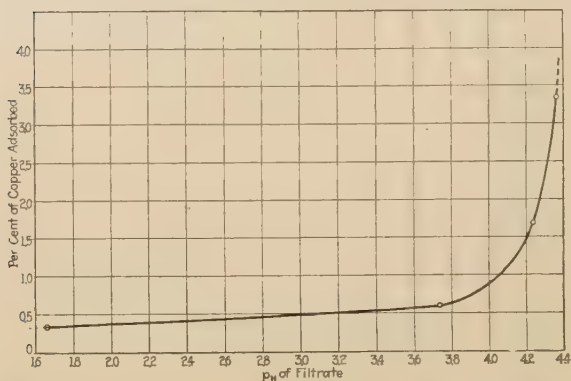


Fig. 4—Change of Copper Adsorption With Acidity of Filtrate

There is a marked decrease in copper adsorbed with increased acidity—the maximum effect occurring at p_H 4 to 3.8.

with sodium carbonate. It was found that as far as copper precipitating power is concerned neither time of heating nor concentration of alkali used is a factor in activating this substance, as is shown in Tables V and VI.

It is evident that recalcining black ash residue with sodium carbonate is not the complete explanation of its very remarkable metal-adsorbing power. The effect of heating other chars with sodium carbonate is shown in Table VII.

The crude chars were prepared by heating the raw materials in a lightly covered iron pan to about 600 deg. C. The crude char was ground and a portion heated with 5 per cent sodium carbonate to 950 deg. C. for 2 hours. This product was washed and dried and constituted the treated chars.

With regard to copper the raw sugar and pine chars are negative adsorbents (concentration of solution increases) and the treatment with sodium carbonate improves them very little.

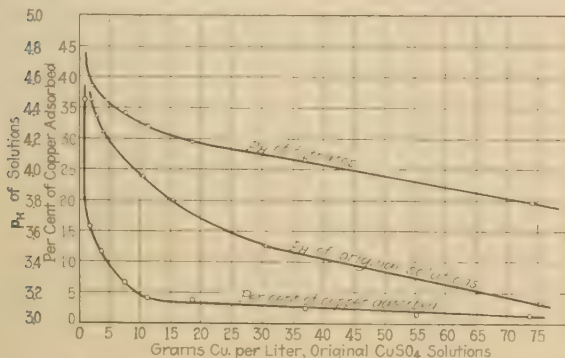


Fig. 5—Change of Copper Adsorption With Original Concentration of Solutions

When the adsorption is less than 5 per cent, there is practically no change with concentration. The p_H of both the original solution and the filtrates is shown in the other curves. They approach each other at about 20 per cent adsorption.

The relative inertness of the sugar and pine char toward activation leads to the belief that black ash residue has been activated during the process of its manufacture and any increase in activity brought about by calcining with alkali is to some extent due to the presence of partly carbonized material. This is shown by the fact that sugar char made at 450 deg. C. and cooled before all vapors have been evolved can be activated partly by heating to 950 deg. C. with alkali. This condition of affairs will not hold for the adsorption of gold from aurocyanide solution, however.

Sugar char prepared by charring a mixture of sugar and sodium carbonate is a soft black material in all ways similar to black ash residue, and is prepared by the same process. Black ash residue is therefore a chance specimen of the more general class of alkaline impregnated chars, the third class of impregnated chars described in the preceding paper. (See *Chem. & Met.*, vol. 32, pp. 13.) The value of this method of activating charcoal for gold adsorption will be discussed in a subsequent article.

Activated Char for Gold Adsorption

A Study of the Various Methods of Activation Revealed a New Class of Carbons Having Unusual Metal-Adsorbing Properties

CARBON has long been advocated as a precipitant for gold from aurocyanide liquors, as the advantages of this agent were early recognized. However, due to erroneous ideas concerning the mechanism of this precipitation, no attempts were made to increase the precipitating power by increasing the adsorptive properties of the charcoal. It is the purpose of this article to draw attention to the manner in which charcoal responds to the various treatments employed for activation for this specific use.

The early investigators (1)* in this field assumed that the gold was reduced by chemical action, and in the case of gold chloride solutions the following reaction was assumed:



But since only about five-hundredths of the theoretical amount of carbon dioxide was evolved, the theory was abandoned. Recent work in this line (2) indicates that any carbon dioxide evolved is simply due to displaced gas liberated by immersion in the solution. If the char is previously boiled with water to eliminate the adsorbed gases, no carbon dioxide is evolved, although the gold is equally well precipitated.

For a time it was believed that cyanide solutions "poisoned" the carbon and that adsorption of gold from such solutions would therefore be impossible. How this idea arose is not clear, as it has since become apparent that gold can be very well removed from aurocyanide solutions by charcoal.

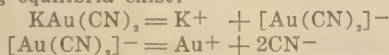
The carbon-monoxide theory (2) was next evolved and has largely held the stage up to the present time. This theory will not be discussed except to note that it has no chemical or experimental foundation, and that removal of carbon monoxide improved the char rather than diminished its precipitating power.

A. W. Allen (*Chem. & Met.*, 1918, vol. 18, p. 642) advanced the hypothesis that the gold is adsorbed in the form of the compound $\text{KAu}(\text{CN})_2$. The reasons advanced by him in support of this idea are entirely

*Numbers refer to references at the end of this article.

valid, but likewise apply to other adsorptive processes. However, this step is in the right direction, as it eliminates the idea of precipitation due to chemical reduction or to the formation of special chemical compounds.

In a solution of AuCN in KCN, among several, the following equilibria exist:



and it is evident that it would be possible to have adsorbed any of the various ions or compounds present. In the preceding articles it has been shown that the adsorption of copper by charcoal decreases when the copper is bound in a complex ion. Thus when a 0.05 molar copper sulphate solution is tested according to the standard procedure, approximately 27 per cent of the copper is removed from solution, whereas only 10 per cent is removed if the solution contains excess ammonia, and only traces of copper are taken up if the solution contains an excess of potassium cyanide. Although the total copper concentration of these solutions is the same in each case, the copper-ion concentration decreases when we add ammonia, and becomes almost negligible when an excess of cyanide is present. It appears, therefore, that as the concentration of the copper ions is decreased the adsorption is decreased, other factors being held constant. This same situation exists with regard to gold salts, as the metal is more easily withdrawn from the chloride solution than from the cyanide. Furthermore, the very stable auric cyanide furnishes so few gold ions that the metal is practically unadsorbed when in solution as the -ic cyanide. The metal is removed from solutions of aurocyanide, however.

PROVING THE THEORY

There is some evidence that metal adsorption by charcoal is a combination of both molecular (equivalent) and ionic (hydrolytic) processes, and that as the metal becomes more noble the hydrolytic becomes the more dominant factor in adsorption. For various reasons, then, it might be expected that gold would precipitate chiefly as the metal from aurocyanide solutions, except at the beginning of adsorption, when a certain amount of compound would be taken up.

In order to test this point experimentally it is neces-

sary to show that the concentration of the cyanide in solution varies in one of two ways:

(a) The cyanide concentration decreases throughout the time of adsorption and proportionally to the amount of gold removed.

(b) Or decreases at first but not during the major portion of the period of adsorption.

If (a) were shown to be true, then the gold is adsorbed as a compound or complex ion as postulated by Allen, but if (b) were demonstrated, then a combination of both equivalent and hydrolytic adsorption is the only explanation.

However, it is not practical to settle these points definitely by any such simple means, since the accuracy of our methods for determining free cyanide will not permit the measurement of the extremely small concentration changes involved. On the large scale the loss of cyanide through oxidation or volatilization is sufficient to render accurate measurement impossible. Hence a different method of proof must be employed.

When a solution of silver nitrate is treated with an alkaline char the silver is precipitated on the char in white metallic form, the char when in suspension having a remarkable luster in contrast to the ordinary

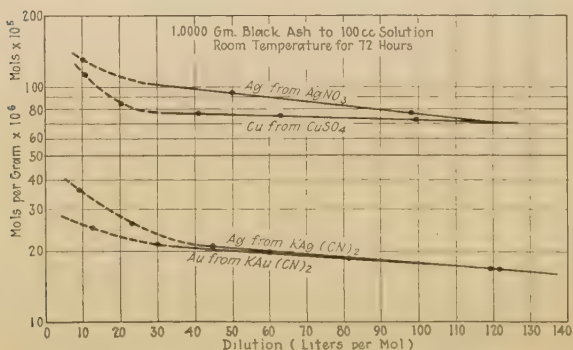


Fig. 1.—Adsorption Curves for Copper, Gold and Silver
From Various Solutions

It will be observed that the greater deviations between silver and copper (from nitrate and sulphate solutions respectively) and silver and gold (from cyanide solutions) occur at the higher concentrations. The different acid radicals may account for the greater deviation between the copper and silver. It will be noted that the gold and silver curves practically overlap except at the higher concentrations.

dull black appearance. This is also observed with gold chloride solutions, the char partaking of a gold-plated appearance. A specimen of char weighing 1.000 gram after having adsorbed 64 mg. of gold from aurocyanide solution also showed the characteristic color of metallic gold. This metal is not extracted from the char by hydrochloric acid. Even in such relatively concentrated solutions as 0.01 molar copper sulphate the acid adsorbed is only about 50 per cent of the equivalent metal adsorbed. This constitutes the first step toward the belief that the gold is adsorbed as the metal from dilute aurocyanide solutions.

In Fig. 1 is plotted the adsorption curves for copper from sulphate solutions, silver from nitrate solutions, and both gold and silver from cyanide solutions. The results are plotted on a semi-logarithmic scale, as this form gives the nearest to a straight-line graph. In plotting the values of the copper adsorbed from the sulphate solution, the analytical values have been multiplied by 2 in order to reduce the data to a monovalent basis of comparison.

It will be noticed that as the solutions tested become less concentrated the metal adsorbed per gram of char, when expressed in mol equivalents, approaches the same value for both copper and silver. The effect of the acid radical, which probably accounts for the deviations observed at higher concentrations, also becomes less. In the case of silver and gold adsorbed from the cyanide solutions, the two curves practically overlap, except at the higher concentrations. The relative amounts of silver adsorbed from the nitrate and cyanide solutions at equivalent concentrations bear the ratio of approximately 50 to 1 and since the two curves are parallel, the actual mechanism of adsorption is likely the same in both solutions—the actual amount of silver adsorbed being proportional to the silver-ion concentration (activity) in the two solutions. Furthermore, in the case of copper it is observed empirically that the valence of the ion comes into consideration, which would not likely be the case unless the copper is adsorbed as the metallic ion. This constitutes the second part of our reasoning in favor of the assumption that both gold and silver are adsorbed chiefly in the metallic state, especially from solutions of low concentrations as are found in commercial cyanide practice. At higher

concentrations there is no doubt that some of the metal is adsorbed in the form of a complex ion or molecule. A commercial cyanide liquor carrying about $\frac{1}{2}$ oz. Troy of gold per ton liquor corresponds to a dilution of nearly 11,500, whereas the most dilute solution we were able to measure accurately corresponded to a dilution of 120. (Fig. 1.)

In preceding articles (see *Chem. & Met.*, vol. 32, Nos. 1 and 2, pp. 13 and 56) it has been indicated that an alkaline-treated char is a very effective metal precipitant. This is a new development, although the effect of alkali on carbon has been known for some time. Haber and Brunner (4) state that wood charcoal dissolves in fused caustic at 500 deg. C. to form carbonate and hydrogen, and Glassner and Suida (5) show that heating wood char with potassium carbonate increases the adsorptive power for the dyes, crystal violet and crystal ponceau. They believed that the effect was due to the formation of cyanide compounds, because the increase was much less when heated with carbonate in a stream of carbon dioxide.

The actual presence of cyanide in these chars has not been demonstrated, hence the effect of carbon dioxide is likely due to the increased stability of the carbonate under such conditions, thus reducing the chemical effect on the surface of the char. Since the peculiar properties of the alkaline chars are not developed by simple treatment with alkaline solutions at the ordinary boiling temperature (or even in an autoclave), it is reasonable to conclude that the surface of the carbon is to some extent modified by the drastic treatment at higher temperatures, either through chemical action or by the adsorption and stabilization of certain ions.

DETERMINING ADSORPTIVE CAPACITY

It is clearly recognized that different kinds of wood yield chars of varying precipitating power. As has been suggested, this may be due to variation in the tannin content of the wood, although the alkaline-ash content is probably a more important factor.

The results obtained in the authors' tests, therefore, are not to be taken as limiting values, but merely as approximations of the way in which charcoal will respond to various methods of treatment intended to improve the precipitating power.

According to Clevenger (6) the limits encountered in cyanide metallurgical practice are about: Free cyanide by "Liebig's test," 0 to 0.25 per cent; gold content, up to 0.5 oz. per ton liquor; silver content, up to 10 oz. per ton liquor. If gold be taken as \$20.67 per oz. and bullion at \$20 per oz., a testing solution containing 0.0171 gram per liter = 0.5 oz. per ton of liquor = \$10 per ton value. Also the lower limit of \$0.02 per ton = 0.000034 gram per liter.

The adsorptive capacity of the char is determined as follows: The sample to be tested, weighing usually 2.0000 grams, is boiled with a small amount of water to expel air and hence prevent channeling, is cooled and poured into a special filter tube, through which the excess water is sucked out. The filter tube is made of glass, $\frac{3}{4}$ in. in diameter with a perforated glass plate fused in place about 7 in. from the end. A glass stopcock is fused to the tube also. A circular piece of canvas is used as the filter cloth. The thickness of the cake varies with the density of the char, but runs from $1\frac{1}{4}$ to 2 in. in thickness. The gold solution is sucked through at a rate of about 400 c.c. per hour. The filtrate passing through is collected and measured. When experience indicates, the filtrate is tested for the gold content. When about 10 per cent of the gold in the testing solution begins to run through in the filtrate, the test is discontinued, the char washed out of the tube, filtered and again placed in position for a continuation of the test. It will be found that a further quantity of gold will be adsorbed before any begins to run through in the filtrate. This procedure is repeated until the solution begins to pass though the char immediately after the sample has been replaced in the tube. The increased capacity due to this procedure is simply due to the fact that new char surface is brought into play each time.

Attempts to revivify the char by sucking air through the moist cake, drying at 100 deg. C. and ignition to red heat were found to be ineffective. In fact, a loaded char after ignition will give up its gold content to the cyanide solution.

CALCULATING AMOUNT OF GOLD ADSORBED

The total amount of gold adsorbed by the char is computed from the volume of solution cleaned. In

order to convert the weight of gold adsorbed into workable units the following factors have been employed: Wt. Au in mg. per gram char $\times 29.2 =$ wt. Au in Troy oz. per short ton char, or $\times 32.6 =$ wt. Au in Troy oz. per long ton char. Also for practical purposes we may multiply the weight of char in grams required to clean a given volume of liquor (liters) by 2 in order to convert to pounds of char required per long ton of liquor of same concentration. Thus, if 1.0000 gram char removes the gold from 2.5 liters of solution, 2 lb. of char will remove the gold from 2.5 tons of liquor of the same concentration.

The method used for determining the amount of gold in the filtrate from the char is briefly as follows: (1) 500 c.c. (or less) sample is placed in a 750-c.c. wide mouth bottle. (2) 15 c.c. saturated solution of sodium cyanide added. (3) 2 drops of saturated lead acetate solution added. (4) 1 gram 200-mesh zinc dust sprinkled in. (5) Shake violently for 2 minutes. (6) Allow precipitate to settle and decant liquor. (7) After washing, transfer precipitate to beaker and digest with dilute hydrochloric acid to remove zinc. (8) Wash residue free from zinc salts. (9) Dissolve residue in 5 c.c. of dilute aqua regia, evaporate to 2 c.c. and cool. (10) Dilute to 10 c.c. in $\frac{3}{4}$ -in. test tube and add stannous chloride dropwise (2 to 5 drops). Color develops in 30 seconds and ranges from slight yellow to pink and blue. The color is fairly stable. It is not necessary to filter out the lead-chloride crystals.

The stannous chloride solution is made by dissolving stannous chloride crystals in 10 per cent hydrochloric acid to give a 12.5 per cent solution, which is preserved over metallic tin. The dilute aqua regia contains 100 c.c. of concentrated hydrochloric acid, 10 c.c. concentrated nitric acid and 100 c.c. water.

The average color range with known amounts of gold is shown in the following table:

0.000050 gram gold...	Looking down tube shows slight pink
0.000100 gram gold.....	Decided pink
0.000300 gram gold.....	Light blue
0.000600 gram gold.....	Dark blue, cannot see down tube
0.001000 gram gold.....	Very dark blue

The best results are obtained in the pink to blue range.

EXPERIMENTS WITH GOLD ADSORBENTS

Experimental data showing the effect of various modes of treatment upon the metal precipitation power of the chars are summarized as follows:

Experiment 1. Material: Leached black ash residue, re-washed and dried. Sample, 2.0000 grams. Sized through 90 mesh and on 100 mesh. Solution 17.15 mg. Au per liter. Free cyanide = 0.26 per cent.

Volume of Filtrate, c.c.	Au Treated, mg.	Au Adsorbed, mg.
1,200	20.58	20.41
700	12.00	11.83
300	5.15	4.98
100	1.71	1.54
Total.....		83.76

Au per gram char = 19.38 mg., or equal to 632 oz. Troy per long ton char.

Experiment No.	Mg. Au Per Gram Char	Troy Oz. Au Per Long Ton Char
2	26.1	850
3	59.52	1,940
4	8.32	271
5	15.95	520
6	25.57	834
7	42.45	1,384

In all experiments 2 to 7, sample used = 2.0000 grams char.

Sample sized to pass 90 mesh and retained on 100 mesh.

Testing solution contained 17.15 mg. Au per liter. Free cyanide by titration = 0.26 per cent.

Treatment of samples previous to testing:

2. Leached black ash residue, heated to 900 deg. C. for 1 hour and quenched hot.

3. Leached black ash residue, heated with sodium carbonate to 900 deg. C. for 2 hours, quenched hot, washed and dried.

4. Crude pine char, heated to 900 deg. C. for 2 hours and cooled in covered crucible.

5. Crude pine char, heated to 900 deg. C. for 2 hours, quenched hot, filtered and dried.

6. Crude pine char, heated with 10 per cent sodium carbonate for 2 hours at 900 deg. C., quenched hot, washed and dried.

7. Pine char made by impregnating pine sawdust with saturated solution of sodium carbonate, and then heating progressively to 900 deg. C. and quenched hot, washed and dried.

DEMONSTRATED VALUE OF ALKALINE CHARS

The preceding experiments 1 to 6 summarized the results of tests on two classes of chars—namely, an alkaline impregnated char (black ash residue) and a

crude primary wood char (pine sawdust char). The results show that the alkaline char is superior at every stage, although the crude pine char after being heated to 900 deg. C. and quenched hot exhibits considerable metal-precipitating power. Treatment with sodium carbonate at about 900 deg. C. followed by hot quenching in water gives products much superior to any hitherto used in commercial cyanide practice. The specially treated black ash residue with a capacity of around 2,000 Troy oz. per ton char is well within the requirements of a commercial char. If the pine sawdust is saturated with sodium carbonate solution before charring and then heated to 900 deg. C., the resultant char is extremely efficient.

Since the best previous results obtained with char in cyanide practice by using a specially quenched and wet ground material (7) range around 770 oz. per ton of char, the beneficial results obtained by treatment with sodium carbonate both before and after charring are clearly illustrated in the preceding table.

Tests made upon solutions containing both silver and gold show that as the metal concentration is increased the break point occurs at slightly lower capacities. However, the total precipitating power is practically unchanged. The results of two tests in this connection may be summarized as follows:

Experiment 8.

Material; black ash residue, heated with 10 per cent sodium carbonate to 900 deg. C. for 2 hours, quenched hot, washed and dried.

Sample 2.0000 grams, sized through 90 and on 100 mesh.

Solution; 17.15 mg. Au and 35.00 mg. Ag per liter.

Free cyanide by titration = 0.27 per cent.

53.96 mg. total metal adsorbed per gram char.

1,759 Troy oz. metal per long ton char.

Silver came through first, no gold in filtrate.

Experiment 9.

Material: same as above.

Sample 4.0000 grams sized as above.

Solution 17.15 mg. Au and 171.5 mg. Ag per liter.

Free cyanide by titration = 0.25 per cent.

39.15 mg. total metal adsorbed per gram char.

1,276 Troy oz. metal per long ton char.

In both experiments 8 and 9 the test was stopped when 10 per cent of the silver in solution appeared in the filtrate. The total capacity to saturation is much

higher, but could not be determined accurately on the small scale.

LARGE-SCALE APPLICATION

The technical problems involved in the adaptation of char for removal of gold and silver from cyanide liquors appear to have been met successfully in hydrometallurgical plants in Australia and South Africa (8). The use of lump charcoal is not feasible, because of the low efficiency and the bulk of material to be smelted. The latest practice involves wet grinding of the char and forming a cake of the ground material on the leaves of a leaf filter. The liquor to be treated is pulled through several units in succession, the strongest liquors meeting the partly loaded char and the weakest liquor the fresh char. The cakes are dropped at intervals and re-formed, bringing new surfaces into action and materially increasing the capacity of the char. After washing and drying, the cakes are burned to remove the carbon, and the ash is collected and smelted with a special flux.

Whether charcoal will replace zinc will be a question of local conditions. When a very foul liquor is being treated, char will be cheaper than zinc under most circumstances, since the bullion is more easily refined and is valued at \$2 to \$3 per ounce higher than that produced with zinc. This is especially true with liquors running high in antimony and arsenic. In isolated localities where wood is plentiful the char process can replace zinc at about one-half the cost. Other factors also influence the choice in certain plants. Among those favoring the use of charcoal are:

(1) The gold can be more completely removed from foul liquors.

(2) Higher grade bullion is produced.

(3) The refining cost is less.

(4) No fouling agent is introduced into the solution.

(5) Cyanide consumption is less.

(6) Cyanide concentration may be less.

In general the advantage to be gained by the use of char are such that with more efficient chars available the industry will undoubtedly take more interest in this very promising new development. The use of black ash residue in this field will afford an outlet for a very troublesome waste product of the paper industry.

However, efficient char can usually be made locally from materials available and at a low cost.

REFERENCES

- (1) Konig, *Chem. News*, vol. 45, p. 215 (1882).
- (2) Green, *Trans. I. Min. & Met.*, vol. 27, p. 316 (1914).
- (3) Allen, *Chem. & Met.*, vol. 18, p. 642 (1918).
- (4) Haber and Brunner, *Z. Elect. Chem.*, vol. 10, p. 697 (1904).
- (5) Glassner and Suida, *Liebig's Ann.*, vol. 357, p. 95 (1907).
- (6) Clevenger, *Trans. Am. Electrochem. Soc.*, vol. 28, p. 263 (1915).
- (7) Edmands, *Bull. Inst. Mining Met.*, London, March, 1918.
- (8) Walton, *Rep. Dept. Mines*, West Australia, 1916.

VITA

Paul McHeehan Horton was born July 28, 1895, in Jackson, Ohio, and received his early education in the public schools of that city. He entered The Ohio State University at Columbus, Ohio, in September of 1914, and received the degree of Bachelor of Chemical Engineering in June, 1918.

Previous to receiving his degree he had enlisted in the National Army in April of 1918 and was stationed in the Dispersoid Division of the Chemical Warfare Service, American University, Washington, D. C., until January of 1919.

From this period until the fall of 1921 he was engaged in industrial work, first with the Minnesota Match Mfg. Co., at Duluth, Minnesota and later with B. F. Drakenfeld & Co., at Washington, Pennsylvania.

In 1921 he was appointed Assistant Professor of Chemistry in The Louisiana State University, Baton Rouge, Louisiana.

Received the degree of M.Sc. in chemistry at Louisiana State University in June, 1923. On leave of absence from the Department of Chemistry, Louisiana State University, during the academic year 1923-1924. He was holder of a Fellowship in Chemical Engineering of the Department of Chemical Engineering in Columbia University.

